Dynamic model-based evaluation of process configurations for integrated operation of hydrolysis and co-fermentation for bioethanol production from lignocellulose

Ricardo Morales-Rodriguez\textsuperscript{a}, Anne S. Meyer\textsuperscript{b}, Krist V. Gernaey\textsuperscript{c}, Gürkan Sin\textsuperscript{a,}\textsuperscript{⇑}

\textsuperscript{a} CAPEC, Dept. of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark
\textsuperscript{b} Center of Bioprocess Engineering, Dept. of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark
\textsuperscript{c} Center for Process Engineering and Technology, Dept. of Chemical and Biochemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark

\textbf{Article info}

\textbf{Article history:}
Received 21 June 2010
Received in revised form 3 September 2010
Accepted 9 September 2010
Available online 17 September 2010

\textbf{Keywords:}
Bioethanol
Process configuration
Hydrolysis and co-fermentation
Dynamic models
SSCF

\textbf{ABSTRACT}

In this study a number of different process flowsheets were generated and their feasibility evaluated using simulations of dynamic models. A dynamic modeling framework was used for the assessment of operational scenarios such as, fed-batch, continuous and continuous with recycle configurations. Each configuration was evaluated against the following benchmark criteria, yield (kg ethanol/kg dry-biomass), final product concentration and number of unit operations required in the different process configurations. The results show that simultaneous saccharification and co-fermentation (SSCF) operating in continuous mode with a recycle of the SSCF reactor effluent, results in the best productivity of bioethanol among the proposed process configurations, with a yield of 0.18 kg ethanol/kg dry-biomass.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Biofuels can potentially contribute to alleviate the current climate change and energy resource challenges, which today’s society is facing. However, turning biofuels production at industrial scale into a success story is only possible by solving a number of challenges. This includes securing a sustainable feedstock supply as well as optimizing the techno-economic feasibility of cellulosic biomass conversion technologies by defining optimal process configurations (Gírio et al., 2010; Huber et al., 2006; Regalbuto, 2009).

Thus far the transfer of these conversion technologies from proof-of-concept to industrial scale has been mainly done on an empirical basis that is typically inefficient and costly in terms of time and resource consumption (Aden et al., 2002; Gnansounou, 2010; Larsen et al., 2008). Although various flowsheet configurations have been reviewed and evaluated in the literature based on steady state models (Alvarado-Morales et al., 2009; Cardona and Sánchez, 2007; Lynd et al., 2008), quantitative modeling tools for the dynamic simulation and evaluation of different process flowsheet options have until now not been used for cellulosic ethanol production processes.

The objective of this work was to develop a Dynamic Lignocellulosic Bioethanol (DLB1.0) modeling platform allowing the quantitative simulation and comparison of different process configurations for 2nd generation (2G) bioethanol plants, thereby providing a basis for evaluation of the most promising process flowsheet. The study has taken a conventional process configuration (Margeot et al., 2009) as a base case using the dimensions and process conditions proposed by Aden et al. (2002). Dynamic models for each unit process operation, including pre-treatment, enzymatic hydrolysis and co-fermentation, have been implemented in one software platform (Matlab Simulink), and connected to obtain the plantwide dynamic model. This dynamic model has subsequently been used to simulate and evaluate different process configurations for 2G bioethanol production on the basis of several benchmark criteria, notably the ethanol yield per unit biomass.

2. Methods

2.1. DLB1.0 mathematical models: pre-treatment, hydrolysis, co-fermentation and simultaneous saccharification and co-fermentation (SSCF)

The model-based simulation framework involved two main parts: (1) the collection, analysis and identification of the most
Nomenclature

ADB  accumulated dry-biomass
C  continuous operation
C_RECY  continuous-recycle operation
Cin,i  concentration of compound i in the feedstream of the unit (g/kg), (g/L)
CA  arabinose concentration (g/kg)
CAM  arabinoxylan concentration (g/kg)
CALS  acid-soluble lignin concentration (g/kg)
CL  lignin concentration (g/kg)
CLE  total enzyme concentration (g/kg)
CE  bound concentration of CHB and EG (g/kg)
CF  free enzyme concentration of CHB and EG (g/kg)
CfXY  free enzyme concentration of β-glucosidase in solution (g/kg)
CETC  ethanol concentration from glucose fermentation (g/kg)
CETXY  ethanol concentration from xylose fermentation (g/kg)
CETG  ethanol concentration above which cells do not grow in xylene fermentation (g/kg)
CX  other compounds concentration (g/kg)
CXy  cell dry weight in xylose fermentation (g/L)
CXG  cell dry weight in glucose fermentation (g/L)
CXY  ethanol concentration from xylose fermentation = 50.40 g/L
CXYG  cell dry weight in xylene fermentation (g/L)
CGL  glucan (cellulose) concentration (g/kg)
CG  glucose concentration (g/kg)
CEL  cellulose concentration (g/kg)
CELX  xylan concentration (g/kg)
CAl  arabinoxylan concentration (g/kg)
CIN  cell dry weight in xylose fermentation (g/L)
CASL  cellulose concentration (g/kg)
CGX  xylose concentration (g/kg)
CFL  lignin concentration (g/kg)
C2  ethanol concentration above which cells do not produce ethanol in glucose fermentation = 60.20 g/L
C2G  ethanol concentration above which cells do not produce ethanol in glucose fermentation = 59.04 g/L
C2XY  ethanol concentration above which cells do not produce ethanol in xylene fermentation = 59.40 g/L
C2Xy  ethanol concentration above which cells do not produce ethanol in xylose fermentation = 59.40 g/L
C2XYG  ethanol concentration above which cells do not produce ethanol in xylene fermentation = 50.40 g/L
C2XyG  ethanol concentration above which cells do not produce ethanol in xylose fermentation = 50.40 g/L
C2GL  ethanol concentration above which cells do not produce ethanol in glucose fermentation = 59.04 g/L
C2XYG  ethanol concentration above which cells do not produce ethanol in xylene fermentation = 50.40 g/L
C2XyG  ethanol concentration above which cells do not produce ethanol in xylose fermentation = 50.40 g/L
CINL  glucan (cellulose) concentration (g/kg)
CFLG  lignin concentration (g/kg)
CFLX  xylan concentration (g/kg)
CFLXY  glucose and xylose mixture = 3.4 g/L
CETXY  concentration of ethanol 1 = 0.4 g/g substrate
CETXY  concentration of ethanol 2 = 0.1 g/g substrate
CETXY  concentration of ethanol 3 = 0.2 g/g substrate
CETXY  concentration of ethanol 4 = 0.067 g/g substrate
CETXY  concentration of ethanol 5 = 0.097 g/g substrate
CETXY  concentration of ethanol 6 = 0.115 g/g substrate
CETXY  concentration of ethanol 7 = 0.162 g/g substrate
CETXY  concentration of ethanol 8 = 0.250 g/g substrate

Greek letters
\( \alpha \)  constant relating substrate reactivity with degree of hydrolysis, 1
\( \beta_1 \)  constant in product inhibition model in glucose fermentation
1.29 for \( Et \leq 95.4 \) g/L, 0.25 for \( 95.4 < Et \leq 129.9 \) g/L
\( \beta_2 \)  constant in product inhibition model in xylene fermentation
1.036 g/L
\( \gamma_1 \)  maximum specific rate of glucose formation
1.42 for \( Et \leq 95.4 \) g/L
\( \gamma_2 \)  maximum specific rate of xylene formation
0.608 g/L
\( \mu_{max,G} \)  maximum specific growth rate in glucose fermentation
0.662 h^{-1}
\( \mu_{max,Xy} \)  maximum specific growth rate in xylene fermentation
0.190 h^{-1}
\( \nu_{max,G} \)  maximum specific rate of glucose formation
2.005 h^{-1}
\( \nu_{max,Xy} \)  maximum specific rate of xylene formation
0.250 h^{-1}

DLB1.0 Dynamic Lignocellulosic Bioethanol model version 1.0

ADB  accumulated dry-biomass
C  continuous operation
C_RECY  continuous-recycle operation
Cin,i  concentration of compound i in the feedstream of the unit (g/kg), (g/L)
CA  arabinose concentration (g/kg)
CAM  arabinoxylan concentration (g/kg)
CALS  acid-soluble lignin concentration (g/kg)
CL  lignin concentration (g/kg)
CLE  total enzyme concentration (g/kg)
CE  bound concentration of CHB and EG (g/kg)
CF  free enzyme concentration of CHB and EG (g/kg)
CF  free enzyme concentration of β-glucosidase in solution (g/kg)
CETC  ethanol concentration from glucose fermentation (g/kg)
CETXY  ethanol concentration from xylose fermentation (g/kg)
CETG  ethanol concentration above which cells do not grow in xylene fermentation (g/kg)
CX  other compounds concentration (g/kg)
CXy  cell dry weight in xylose fermentation (g/L)
CXG  cell dry weight in glucose fermentation (g/L)
CGL  glucan (cellulose) concentration (g/kg)
CG  glucose concentration (g/kg)
CEL  cellulose concentration (g/kg)
CELX  xylan concentration (g/kg)
CFL  lignin concentration (g/kg)
CFLG  lignin concentration (g/kg)
CFLX  xylan concentration (g/kg)
CFLXY  glucose and xylose mixture = 3.4 g/L
CETXY  concentration of ethanol 1 = 0.4 g/g substrate
CETXY  concentration of ethanol 2 = 0.1 g/g substrate
CETXY  concentration of ethanol 3 = 0.2 g/g substrate
CETXY  concentration of ethanol 4 = 0.067 g/g substrate
CETXY  concentration of ethanol 5 = 0.097 g/g substrate
CETXY  concentration of ethanol 6 = 0.115 g/g substrate
CETXY  concentration of ethanol 7 = 0.162 g/g substrate
CETXY  concentration of ethanol 8 = 0.250 g/g substrate

Greek letters
\( \alpha \)  constant relating substrate reactivity with degree of hydrolysis, 1
\( \beta_1 \)  constant in product inhibition model in glucose fermentation
1.29 for \( Et \leq 95.4 \) g/L, 0.25 for \( 95.4 < Et \leq 129.9 \) g/L
\( \beta_2 \)  constant in product inhibition model in xylene fermentation
1.036 g/L
\( \gamma_1 \)  maximum specific rate of glucose formation
1.42 for \( Et \leq 95.4 \) g/L
\( \gamma_2 \)  maximum specific rate of xylene formation
0.608 g/L
\( \mu_{max,G} \)  maximum specific growth rate in glucose fermentation
0.662 h^{-1}
\( \mu_{max,Xy} \)  maximum specific growth rate in xylene fermentation
0.190 h^{-1}
\( \nu_{max,G} \)  maximum specific rate of glucose formation
2.005 h^{-1}
\( \nu_{max,Xy} \)  maximum specific rate of xylene formation
0.250 h^{-1}
promising mathematical models for pre-treatment, enzymatic hydrolysis and co-fermentation, and (2) the design, simulation and comparison of different integrated operational scenarios such as, fed-batch, continuous and continuous-recycle (Sin et al., 2010). The chosen configurations employ separate hydrolysis and fermentation (SHEF), where – as the name implies – the enzymatic hydrolysis as well as the fermentation has been performed in different unit operations. In addition, a model for the simultaneous saccharification and co-fermentation (SSCF) process was developed and configurations including SSCF reactors were simulated and compared with the results from the base case.

2.1.1. Pre-treatment

The mathematical model for the pre-treatment process (see Supplementary data (S.1)), which is the operation aiming at breaking down the structure of the lignocellulosic matrix of the raw biomass, has been taken from Lavarack et al. (2002).

2.1.2. Enzymatic hydrolysis

Among many competing models, the mathematical model developed by Kadam et al. (2004) (see Table 1) has been chosen to describe the enzymatic hydrolysis of lignocellulosic biomass, as it has already been extensively analyzed statistically (Sin et al., 2010), verified experimentally (Hodge et al., 2009) and has also been the subject of a thorough model validation (Morales-Rodriguez et al., 2010). The model of Kadam et al. (2004) quantifies the enzyme catalyzed decomposition of the cellulose content in the biomass, where cellulose decomposes to cellobiose (Eq. (1)) and glucose (Eq. (2)) by the action of the enzymes endo-1,4-glucanases + exoglucanases (cellulohydrolases), cellobiose is hydrolyzed to glucose (Eq. (3)) by β-glucosidases, and where the model also accounts for the enzyme adsorption (Eq. (4)), the levels of free and bound enzyme (Eq. (5)), the substrate reactivity (Eq. (6)), and the effect of the temperature on the saccharification modeled by the Arrhenius equation (Eq. (7)). The mathematical model also takes into account the potential inhibition by cellobiose, glucose, and xylose on the different rate constants (Kadam et al., 2004). It is important to note that xylose is a product of the pretreatment section, which is transported in the slurry to the hydrolysis reactor (see supplementary data (S.1)).

2.1.3. Co-fermentation

The mathematical model employed in this work for the co-fermentation process has been proposed by Krishnan et al. (1999) (see Table 2) and considers the simultaneous conversion of xylose and glucose to ethanol. Based on new research findings that indicate that conversion of 5-carbon sugars has become possible via novel recombinant microorganisms, this work considers bio-ethanol production from the conversion of both xylose and glucose to ethanol as a reliable future scenario (Bettiga et al., 2009). The co-fermentation model is based on the recombinant yeast Saccharomyces cerevisiae strain 1400 (pNLH3). The use of this yeast as the fermenting organism differs from the NREL model (Aden et al., 2002) that uses Zyymomonas mobilis for the glucose and xylose fermentation in a series of different anaerobic batch fermentors.

The mathematical model for co-fermentation involves the reaction rates for: (1) cell growth on glucose (Eq. (12)) and xylose (Eq. (13)); (2) the total yeast cell mass production as the average product of the cell growth on glucose and xylose using the respective mass fraction of these compounds present in the mixture (Eq. (14)); (3) consumption of glucose (Eq. (15)) and xylose (Eq. (16)); (4) formation of ethanol from glucose (Eq. (17)) and xylose (Eq. (18)); and (5) overall formation of ethanol (Eq. (19)). The model accounts for substrates and product inhibition as well as the effect of the inoculum size that is employed for the cultivation.

For the sake of simplicity a detoxification step was not included after the pre-treatment; neither was the formation and removal of gyspum – as considered in the NREL model (Aden et al., 2002) – included in the dynamic model.

2.1.4. Simultaneous saccharification and co-fermentation (SSCF) model

The development of the reaction kinetics for the simultaneous saccharification and co-fermentation model has been carried out by combining the enzymatic hydrolysis and co-fermentation models described above (Morales-Rodriguez et al., in press). It is known that the presence of ethanol during enzymatic hydrolysis can induce a certain level of inhibition on cellulose degradation as pointed out by Bezerra and Dias (2005). However, for ethanol concentrations less than 4 M (equivalent to 18.42% wt/v ethanol) no significant inhibition of ethanol on the enzymatic activities in the saccharification has been found (Ooshima et al., 1985). Moreover, Philippidis et al. (1993) have shown that the value of the inhibition coefficient of ethanol on cellulose (conversion to cellobiose) is approximately 10 times higher than the inhibition coefficient of cellobiose on cellulose conversion. Therefore, in this study, the value of the inhibition constant of cellulose (K_{IEH} ^{C_G}) proposed by Kadam et al. (2004) for the enzymatic hydrolysis of cellulose to cellobiose has been multiplied by a factor 10 in order to obtain the inhibition constant for ethanol. The potential inhibition of ethanol on the enzymatic hydrolysis of cellulose to glucose was neglected as it is assumed insignificant (Bezerra and Dias, 2005).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Kinetic expressions of the enzymatic hydrolysis model (Kadam et al., 2004).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cellulose to cellobiose (g/kg h)</strong></td>
<td>( r_{1,EH} = \frac{\theta_{EH,0} G_c R_1 R_2}{1 + K_{CF} C_{XXy}} ) (Eq. (1))</td>
</tr>
<tr>
<td><strong>Cellulose to glucose (g/kg h)</strong></td>
<td>( r_{2,EH} = \frac{\theta_{EH,0} G_c R_1 R_2}{1 + K_{CF} C_{XXy}} ) (Eq. (2))</td>
</tr>
<tr>
<td><strong>Cellobiose to glucose (g/kg h)</strong></td>
<td>( r_{3,EtG} = \frac{\theta_{EtG,0} G_c R_3}{1} ) (Eq. (3))</td>
</tr>
<tr>
<td><strong>Enzyme adsorption (g/kg h)</strong></td>
<td>( C_{Ea} = \frac{\theta_{EA} G_c}{1 + K_{EA} C_{XXy}} ) (Eq. (4))</td>
</tr>
<tr>
<td><strong>Enzyme (g/kg)</strong></td>
<td>( C_{E} = C_{Ea} + C_{Eb} ) (Eq. (5))</td>
</tr>
<tr>
<td><strong>Substrate reactivity</strong></td>
<td>( R_s = \frac{G_c}{C_{EH}^{1/2} + C_{XXy}} ) (Eq. (6))</td>
</tr>
<tr>
<td><strong>Temp. dependence</strong></td>
<td>( \frac{R_s}{R_s^{30 \text{°C}}} = 0.03 ) (Eq. (7))</td>
</tr>
<tr>
<td><strong>Cellulose kinetic (g/kg h)</strong></td>
<td>( r_{1,EH} = \frac{1}{3 + \theta_{EH,0} G_c R_1 R_2} ) (Eq. (8))</td>
</tr>
<tr>
<td><strong>Cellulose kinetic (g/kg h)</strong></td>
<td>( r_{2,EH} = \frac{1}{3 + \theta_{EH,0} G_c R_1 R_2} ) (Eq. (9))</td>
</tr>
<tr>
<td><strong>Glucose kinetic (g/kg h)</strong></td>
<td>( r_{3,EtG} = \frac{1}{3 + \theta_{EtG,0} G_c R_3} ) (Eq. (10))</td>
</tr>
<tr>
<td><strong>Water kinetic (g/kg h)</strong></td>
<td>( r_{w,EtG} = -0.05 \frac{r_{1,EtG}}{1 + 0.98 \frac{r_{1,EtG}}{r_{1,EtG}}} ) (Eq. (11))</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Kinetic expressions of the co-fermentation model (Krishnan et al., 1999).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Biomass</strong></td>
<td>( \rho_{B,G} = \frac{\rho_{B,G,0} G_c}{1 + K_{BG} C_{EtG}} ) (Eq. (12))</td>
</tr>
<tr>
<td><strong>Biomass</strong></td>
<td>( \rho_{B,Xy} = \frac{\rho_{B,Xy,0} G_c}{1 + K_{BXy} C_{EtG}} ) (Eq. (13))</td>
</tr>
<tr>
<td><strong>Biomass kinetic</strong></td>
<td>( r_{3,EtG} = \frac{\rho_{B,G} G_c}{1 + K_{BG} C_{EtG}} ) (Eq. (14))</td>
</tr>
<tr>
<td><strong>Glucose kinetic</strong></td>
<td>( \rho_{G,G} = \frac{\rho_{G,G,0} G_c}{1 + K_{CG} C_{EtG}} ) (Eq. (15))</td>
</tr>
<tr>
<td><strong>Glucose kinetic</strong></td>
<td>( \rho_{G,Xy} = \frac{\rho_{G,Xy,0} G_c}{1 + K_{CXy} C_{EtG}} ) (Eq. (16))</td>
</tr>
<tr>
<td><strong>Ethanol</strong></td>
<td>( r_{3,EtG} = \frac{\rho_{G,G} G_c}{1 + K_{CG} C_{EtG}} ) (Eq. (17))</td>
</tr>
<tr>
<td><strong>Ethanol</strong></td>
<td>( \rho_{E,G} = \frac{\rho_{E,G,0} G_c}{1 + K_{CE,G} C_{EtG}} ) (Eq. (18))</td>
</tr>
<tr>
<td><strong>Ethanol kinetic</strong></td>
<td>( r_{E,G} = \frac{\rho_{E,G} G_c}{1 + K_{CE,G} C_{EtG}} ) (Eq. (19))</td>
</tr>
</tbody>
</table>
2005; Philippidis et al., 1993). Thus, only the mathematical expression for cellulose decomposition to cellobiose (Eq. (1)) has been modified by adding an additional ethanol inhibition factor $C_E/K_{IEt}$ as shown in Eq. (20).

$$r_{1, EH} = \frac{k_{DH} C_{Et} K_{IEt} C_G}{1 + \frac{C_E}{K_{IEt}} + \frac{C_I}{K_{CEt}} + \frac{C_H}{K_{CEt}}}$$

(20)

The units of model components are different in the separate hydrolysis (g/kg) and co-fermentation models (g/L) (see above). To resolve this issue, it is assumed in the mathematical model for the SSCF process that the density of the mixture is equal to 1 kg/L, such that the models can be integrated.

2.2. Mass balances

This study has employed fed-batch and continuous operations for hydrolysis, co-fermentation and SSCF units, and the generic mass balance for the different compounds present in the unit operations involved in the process is represented as follows:

$$V \frac{dC_i}{dt} = Q_{in} C_{in,i} - Q_{out} C_i + r_{ij} V - C_i \frac{dV}{dt}$$

(21)

where, $Q_{in}$ and $Q_{out}$ are the feed flow rate and outlet flow rate, respectively. $C_{in,i}$ is the concentration of compound $i$ in the feed, $r_{ij}$ is the rate of generation (+)/degradation (−) of compound $i$ in the reaction for the $j$ unit operation, $V$ is the reactor volume, and $C_i$ is the actual concentration of compound $i$ in the reactor, which will be equal to the concentration in the outlet during the drawing period of the reactor. As far as reaction volume is concerned, this is described as follows:

$$\frac{dV}{dt} = Q_{in} - Q_{out}$$

(22)

For fed-batch operation, $Q_{in}$ is different from zero during the loading period and $Q_{out}$ is different from zero for the drawing time. With respect to the continuous operation, $Q_{in}$ and $Q_{out}$ are assumed to be identical during the operation of the enzymatic hydrolysis, co-fermentation and SSCF units, i.e. constant tank volume is assumed.

The mathematical model for the solid–liquid separation assumes an ideal separation in steady state. More details about the model can be found in the Supplementary data (S.2).

3. Results and discussion

3.1. Process technology configurations: upstream

A number of process configurations have previously been proposed for bioethanol production (Aden et al., 2002; Cardona and Sánchez, 2007; Larsen et al., 2008; Lynd et al., 2008; Margeot et al., 2009; Shell et al., 2004). Recently, Dutta et al. (2010) proposed the reconfiguration of the flowsheet presented by Aden et al. (2002) comparing the capabilities of different microorganisms for sugar fermentation as well as including a techno-economic study based on data from bench-scale experiments.

3.1.1. Base case: conventional bioethanol process flowsheet

In this study, a conventional process configuration (Margeot et al., 2009) has been used as a base case (see Fig. 1a). This process configuration consists of four main sections: pre-treatment, enzymatic hydrolysis, fermentation and downstream processes. First of all, the feedstock is treated in the pre-treatment section (using diluted acid pre-treatment), and the product from this operation is passed to the enzymatic hydrolysis unit to perform the conversion of cellulose biomass to glucose. Afterwards, the effluent leaving the enzymatic hydrolysis unit passes through the solid–liquid separator where a percentage of solids is sent to the power generation section (not shown in Fig. 1a), while the liquor stream is sent to the fermentation to ferment the sugars into ethanol. The output stream from the fermentation unit is then transferred to the downstream operations to separate the most valuable products (ethanol) and recover those compounds that can be reused in the upstream sections – especially water.

3.1.2. SHF: Operational scenarios

The SHF process design for the hydrolysis and fermentation processes is investigated using nine different configurations which refer to various combinations of fed-batch (FB), continuous (C) and continuous-recycle (C_RECY) operations (Figs. 1 and 2).

3.1.2.1. Fed-batch enzymatic hydrolysis with fed-batch, continuous and continuous-recycle operation in the co-fermentation reactors. This section describes the three process configurations which employ fed-batch operation in the enzymatic hydrolysis units followed by fed-batch, continuous or continuous-recycle operations in the co-fermentation units (Fig. 1a–c, respectively). Fed-batch operation (see Fig. 1a) in the co-fermentation reactor is similar to the base case described in Section 3.1.1. When the co-fermentation reactors are working in the continuous mode, (Fig. 1b) the liquor leaving the solid–liquid separator is distributed by a stream separator ("splitter" in Fig. 1) to the reactors where the conversion of sugars into ethanol is accomplished. The continuous-recycle configuration (Fig. 1c) operates similarly to the continuous operation (Fig. 1b), but the addition of two more unit operations per fermentor, one mixer and one settler tank, is necessary. The settler tank separates the solids from the liquids in the effluent of the fermentor by gravity settling and recycles the solids back to the mixer unit which also contains the yeast. This recycling ensures that a high concentration of solids is maintained in the co-fermentation reactors.

3.1.2.2. Continuous enzymatic hydrolysis with fed-batch, continuous and continuous-recycle operation in the co-fermentation reactors. Continuous operation in the enzymatic hydrolysis section combined with the co-fermentation step working either in fed-batch, continuous or continuous-recycle mode is also investigated (see Fig. 1d–f, respectively). With enzymatic hydrolysis in batch mode as a reference (Fig. 1a–c), continuous operation requires less unit operations to handle the biomass flow rate from the pre-treatment section in order to fulfill the necessary residence time in the hydrolysis reactors. Co-fermentation reactors are operated in the same manner as described in Section 3.1.2.1. However, some differences are found in other parts of the process flowsheet. For example, in the co-fermentation reactors operating in fed-batch mode (Fig. 1d), the liquor generated by the solid–liquid separator is fed to the co-fermentation reactors until reaching their maximum capacity while the remaining amount is stored in the buffer tank. For continuous (Fig. 1e) and continuous-recycle operation (Fig. 1f) of the fermentors, the effluent from the solid–liquid separator is conveyed directly to the co-fermentation section, thus avoiding the use of the separator unit ("splitter") whether it is compared with the configurations illustrated in Fig. 1b and 1c.

3.1.2.3. Continuous-recycle enzymatic hydrolysis with fed-batch, continuous and continuous-recycle operation in the co-fermentation reactors. Another process configuration in the enzymatic hydrolysis section is based on the recycle of the insoluble solids stream from the solid–liquid separator (Fig. 2a–c). This recycle stream is then mixed with the effluent generated in the pre-treatment section before entering the hydrolysis reactor. After solid–liquid separation,
the configurations for fed-batch (Fig. 2a), continuous (Fig. 2b) and continuous-recycle (Fig. 2c) in the co-fermentation section, are working in a similar manner as described in Section 3.1.2.2.

3.1.3. SSCF operational scenarios

Three different configurations are proposed for the integration of enzymatic hydrolysis and co-fermentation in the same unit.
operation (Fig. 2d–f). During fed-batch operation of the SSCF unit (illustrated in Fig. 2d), this unit is fed continuously with the effluent that is leaving the pre-treatment section. The effluent from the SSCF reactor passes through a solid–liquid separator where the liquor is sent onwards to the downstream processing section, and the solids are collected for subsequent power generation (not shown).

Continuous operation is also investigated for the SSCF unit operation (see Fig. 2e) where the output stream from the pre-treatment process is split into three parts to feed the three parallel SSCF
units. Afterwards, a solid–liquid separation is carried out where the resulting liquid stream is sent to the downstream processing section to perform the recovery and purification of the ethanol. On the other hand, the solid streams are sent to the power generation section for combustion.

Another configuration includes the recycle of the insoluble solids stream to the SSCF unit (see Fig. 2f). This stream is mixed with the liquid stream from the pre-treatment unit. This action aims to produce the highest possible yield of ethanol per amount of processed raw biomass material, thereby reducing the waste of raw materials in the biofuel production plant.

3.1.4. Scheduling for operational scenarios

When fed-batch processes are used (Figs. 1a–d, 2a and 2d), it is assumed that parallel fed-batch reactors are operated following a batch scheduling scheme consisting of a sequence of different operational phases – for example fill, react, draw, idle – that are repeated over time.

The schedule for fed-batch operation (see Fig. 3a) describing the operation of the hydrolysis and co-fermentation units (used in the configuration in Fig. 1a) can be understood as follows: for reactor number one a cycle of operation lasts 60 h. It starts with the loading, an operation that takes 12 h, and is followed by 36 h of reaction time. Finally it ends with 12 h of drawing/emptying the reactor contents. Upon the completion of the first cycle, the next cycle starts again by repeating the same schedule. The first fermentation reactor therefore starts after 48 h then following the 12, 36 and 12 h scheduling (Fig. 3a).

Regarding the co-fermentation unit, the loading period is assumed to start simultaneously with the drawing of the contents from the hydrolysis unit, thus assuming that an ideal solid–liquid separation operating in steady state is present between hydrolysis and co-fermentation. Some configurations (Figs. 1d and 2a) just employ the scheduling strategy (shown in Fig. 3b) for the co-fermentation unit since the hydrolysis is operating in continuous mode. It is important to remark that a buffer tank is needed after the hydrolysis units (operating in continuous) to buffer the continuous flow before it is fed to the fed-batch operated fermentors. Similarly, when the SSCF configuration is operated in fed-batch mode (Fig. 2d) it also uses the scheduling strategy outlined in Fig. 3b, since in this configuration the effluent from the pre-treatment section is directly fed to the SSCF units.

3.2. Process characteristics data and simulation platform used for simulations

Process characteristics and information regarding the dimension of the units have been taken from Aden et al. (2002) (see Table 3). The DLB1.0 simulation of the proposed process flowsheet for bioethanol production has been solved using the MatLab/Simulink (R2008b) platform (The Mathworks, Natick, MA). The MatLab code is available upon request from the authors.

3.3. Results: technological evaluation

3.3.1. Benchmark criteria for comparison of the DLB1.0 simulation of the configurations

The comparison of the performance of the different process flowsheets has been performed by using as evaluation criteria: the maximum ethanol/dry-biomass ratio, the minimum fraction of unreacted raw material and the maximum final ethanol concentration.

3.3.1.1. Mathematical expressions for the ethanol/dry-biomass ratio and unreacted raw material fraction.

The ethanol/dry-biomass ratio has been calculated on the basis of the total amount of ethanol that is transferred to the downstream processing section as follows:

\[ R_{Et/dry-biomass} = \frac{\text{Total Mass } Et}{\text{Total Mass Dry Biomass}} \]  

The fraction of unreacted raw material (URM) has been calculated using the accumulated dry-biomass (ADB) in the process plus the dry-biomass separated in the solid–liquid separator unit versus the total amount of dry-biomass fed in the operating time (Eq. (24)):

\[ URM = \frac{ADB + \text{Solid stream from S–L separator}}{\text{Total Mass Dry Biomass}} \]
Table 3
Main process characteristic and conditions for the simulation of the different process configurations.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Value</th>
<th>Pretreatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock</td>
<td>Corn stover</td>
<td>Reactive</td>
</tr>
<tr>
<td>Operating time considered for</td>
<td>348 h</td>
<td>Concentration % (wt/v)</td>
</tr>
<tr>
<td>the evaluation</td>
<td></td>
<td>1.1</td>
</tr>
<tr>
<td>Glucan</td>
<td>37.4</td>
<td>Residence time</td>
</tr>
<tr>
<td>Xylan</td>
<td>21.1</td>
<td>2 min</td>
</tr>
<tr>
<td>Arabinan</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>Lignin</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>Other compounds</td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td>Enzymatic hydrolysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>338 K</td>
<td>Co-fermentation</td>
</tr>
<tr>
<td>Initial solid concentration%</td>
<td>20</td>
<td>Temperature</td>
</tr>
<tr>
<td>Size of the vessels</td>
<td>3596 m³ (each)</td>
<td>Inoculum level</td>
</tr>
<tr>
<td>Number of vessels</td>
<td>5</td>
<td>10%</td>
</tr>
<tr>
<td>Enzyme</td>
<td>Cellulases (EG, CBH and BDG)</td>
<td>Number of vessels</td>
</tr>
<tr>
<td>SSFC</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Temperature</td>
<td>308 K</td>
<td>Solid–liquid separator</td>
</tr>
<tr>
<td>Inoculum level</td>
<td>10%</td>
<td>Solid separator efficiency</td>
</tr>
<tr>
<td>Size of the vessels</td>
<td>3596 m³ (each)</td>
<td>Percent of water content in the</td>
</tr>
<tr>
<td>Number of vessels</td>
<td>5</td>
<td>insoluble solid stream</td>
</tr>
<tr>
<td>Enzymes</td>
<td>Cellulases (EG, CBH and BDG)</td>
<td>50%</td>
</tr>
<tr>
<td>Organism</td>
<td>Saccharomyces cerevisiae strain1400</td>
<td>(pLNH33)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feature</th>
<th>Value</th>
<th>Diluted sulfuric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of the vessels</td>
<td>3596 m³ (each)</td>
<td></td>
</tr>
<tr>
<td>Enzymes</td>
<td>Cellulases (EG, CBH and BDG)</td>
<td></td>
</tr>
<tr>
<td>Organism</td>
<td>Saccharomyces cerevisiae strain1400</td>
<td>(pLNH33)</td>
</tr>
</tbody>
</table>

3.3.2. Comparison of the DLB1.0 simulations of the configurations based on: ratio ethanol/dry-biomass, unreacted raw material fraction and ethanol concentration

Among the different DLB1.0 simulations of the configurations, the maximum ethanol yield obtained is found for the SSCF process configuration operated with continuous feed with recycling of the solids (see Fig. 2f). This outcome can be explained to a large extent by the positive effect of the recycle, which improves the process efficiency in two ways: (i) by recycling the unused raw material (that is cellulose) the amount of raw material wastage is decreased – this is illustrated in Table 4 – where the amount of unreacted raw material for the SSCF-C_RECY is 0 and (ii) by recycling the yeast, the concentration of microorganisms maintained in the reactor is increased significantly to 9.75% (wt/v) in comparison to 2.13% (wt/v) in the SSCF-C configuration.

The second best yield was found for a SHF type process where both the hydrolysis and the co-fermentation units are operated continuously with recycle (C_RECY-C_RECY) (Fig. 2c). This result demonstrates also that continuous operation with a recycle has the major positive impact among the process flowsheet configurations.

The third best yield was found for a SHF type process configuration where hydrolysis is operated continuously with recycle while the co-fermentation is just in continuous mode (C_RECY-C) (Fig. 2b). The 0.0245 kg ethanol/kg dry-biomass decrease in the ethanol yield is attributable to the lack of recycle in the co-fermentation reactor. Compared to the scenario with the best performance, there is 5.5% of the glucose and 71.2% of the xylose unfermented (with respect to the feed) in the effluent of the fermentor.

The SSCF fed-batch (SSCF-FB) (Fig. 2d) operation is ranked fourth, even though a certain fraction of unreacted raw material is presented (0.13). This configuration presents the highest ethanol concentration (5.8% wt/v) in the final amount of product.

Fed-batch operation for the conversion of cellulose to glucose and continuous operations with a recycle stream in the co-fermentation of glucose and xylose to ethanol (FB-C_RECY, Fig. 1c), is the option ranking 5th among the tested configurations (0.13 kg ethanol/kg dry-biomass). Although SSCF-FB and FB-C_RECY give the same ethanol/dry-biomass yield, the final ethanol concentration in the FB-C_RECY configuration is slightly lower (5.6% wt/v).

The remaining process flowsheet configurations were found to perform poorly with yields below 0.11 kg ethanol/kg dry biomass.

Fed-batch operation inherently involves some transient accumulation of reaction products in the process, which requires a dynamic model to enable proper analysis of the process performance (see Supplementary data (S.3)). Moreover the implication of accumulation of reaction products in the process is that it reduces the total amount of treated biomass during the operation period (see Table 4).

Although the final ethanol concentration obtained from the SSCF-FB (Fig. 2d) was slightly higher (5.8% wt/v) than that obtained with the SSCF-C_RECY (5.5% wt/v) (Fig. 2f), the ratio of ethanol to dry biomass was markedly higher in the SSCF-C_RECY configuration (0.18 kg/kg), which makes SSCF-C_RECY a better alternative (Table 4). The ethanol concentration from FB-C_RECY (Fig. 1c) was also relatively high (5.6% wt/v) but the unreacted raw material was also high (0.14) making it less effective compared to the SSCF-C_RECY configuration. Something similar is observed in the final ethanol concentration (5.5% wt/v) for the FB-FB (Fig. 1a) configuration, which also has slightly lower ethanol/dry-biomass ratio (0.10 kg/kg).

A mass balance summary for the stream that is sent to the downstream processes for the diverse proposed process configurations is included in the Supplementary data (S.4).

3.3.3. Reduction of the number of unit operations for the FB–FB configuration

Specifically for fed-batch operation, an additional simulation study has been performed for both enzymatic hydrolysis and co-fermentation units with the aim of evaluating whether it would be possible to reduce the amount of unit operations (from five reactors in parallel to three reactors in parallel) without compro-
mising the ethanol production. This implicitly involves reduction of the reaction time to 12 h rather than 36 h.

A comparison between both operational scenarios is shown in Table 5. The results show lower values of unreacted raw material in the process with three parallel reactors, indicating more conversion of the raw material in the operating time, which is directly related to the accumulation fraction of raw material in both configurations. Moreover the ethanol/dry-biomass ratio is basically the same for both configurations, meaning that the shorter reaction period is sufficient to obtain a high conversion of the lignocellulosic biomass to ethanol. This indicates that the five reactors based NREL design is too conservative. In other words, the safety factor in the NREL design is too high, since using only three reactors would have been sufficient on the basis of the dynamic model simulations. However, it is also important to highlight the differences in the process configuration in the NREL report and this case study. For example, the NREL report has employed simultaneous saccharification and fermentation (SSF) with an additional reactor volume versus ethanol/dry-biomass ratio

Table 4
Summary of the simulation results for the proposed configurations: ethanol/dry-biomass ratio, unreacted raw material fraction, and ethanol concentration.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>FB-FB</th>
<th>FB-C</th>
<th>FB-C_RECY</th>
<th>C-FB</th>
<th>C-C</th>
<th>C-C_RECY</th>
<th>C_RECY-FB</th>
<th>C_RECY-C</th>
<th>C_RECY-C_RECY</th>
<th>SSCF-FB</th>
<th>SSCF-C</th>
<th>SSCF-C_RECY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol/dry-biomass ratio (kg/kg)</td>
<td>0.10</td>
<td>0.10</td>
<td>0.13</td>
<td>0.09</td>
<td>0.11</td>
<td>0.11</td>
<td>0.10</td>
<td>0.14</td>
<td>0.16</td>
<td>0.13</td>
<td>0.12</td>
<td>0.18</td>
</tr>
<tr>
<td>Unreacted raw material fraction</td>
<td>0.25</td>
<td>0.14</td>
<td>0.14</td>
<td>0.11</td>
<td>0.00</td>
<td>0.00</td>
<td>0.37</td>
<td>0.00</td>
<td>0.00</td>
<td>0.14</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Ethanol concentration % (wt/v)</td>
<td>5.5</td>
<td>4.7</td>
<td>5.6</td>
<td>4.3</td>
<td>4.4</td>
<td>4.5</td>
<td>4.5</td>
<td>4.2</td>
<td>4.9</td>
<td>4.5</td>
<td>4.6</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 5
Results for the FB–FB configuration using five and three operation units.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>FB(5)–FB(5)</th>
<th>FB(3)–FB(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol/dry-biomass ratio</td>
<td>0.10</td>
<td>0.11</td>
</tr>
<tr>
<td>Accumulation fraction in the process</td>
<td>0.25</td>
<td>0.12</td>
</tr>
<tr>
<td>Loading (h)</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Reaction period (h)</td>
<td>36</td>
<td>12</td>
</tr>
<tr>
<td>Drawing (h)</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>

3.4. General discussion

This study integrated, argued and demonstrated the use of a matlab based modeling platform, DLB1.0, for comparative evaluation of the operation and synergy among fed-batch, continuous and continuous with recycle units. The DLB1.0 modeling platform also allows the implementation and evaluation of plantwide control scenarios for the optimized operation. Moreover it enables studying transient and dynamic response of the plants to different disturbances (e.g. varying feedstock composition or varying flow levels).

One of the other contributions in this study is the introduction of one mathematical model for SSCF unit operation, which is built having a combination of the enzymatic hydrolysis and co-fermentation models. The proposed model takes into account the inhibition of ethanol on enzymatic conversion of cellulose, which requires further experimental validation. The DLB1.0 simulations identified five configurations, four of them involving a recycle flow as being the most feasible for maximizing the ethanol yields on a set amount of lignocellulose raw material (Table 4). Recycling of material results in maximizing the enzyme reaction time and fermentation time within a certain processing period. In turn, this allows for full reaction of the raw material in the reactors and thus achieves higher yields for both the enzyme catalysis reaction and the fermentation.

The advantages of technology evaluation based on the DLB1.0 simulations can be seen from three different perspectives: (a) maximize the yield of the raw material, (b) the optimized operation point of view: get more out of the existing plant capacity/equipment, and (c) the process design point of view: use a minimum capacity/equipment to achieve better process performance (design target), which has a direct impact on the capital cost of the bioethanol plant.
One assumption in this study is that there is no inhibition of byproducts (such as, furfural and hydroxy methyl furfural) resulting from the pre-treatment operations to the enzymatic hydrolysis and co-fermentation units implying a detoxification unit before these units operation. This study also assumes no significant changes on the metabolic capacity as a result of the possible accumulation of inhibitors where some recycles are found in the configurations. These are deemed acceptable assumptions as recent molecular and protein engineering research efforts have demonstrated promising results with respect to improving the inhibition tolerance of enzymes used for the hydrolysis as well as the co-fermentation organisms used for fermenting sugars (Almeida and Hahn-Hägerdal, 2009; Bettiga et al., 2009; Karhumaa et al., 2007).

Last but not least, dynamic modeling has been demonstrated to be a promising tool in evaluating different process configurations in view of supporting process design and operation activities. The present work provides a basis that may be expanded to include downstream processing energy/heat integration as well as solids/lignin combustion for power co-generation. In addition, cost analysis and optimization of the process operation and design will also be investigated in order to maximize the yield of bioethanol and reduce the energy consumption in the process.

4. Conclusion

A number of scenarios have been proposed, analyzed and compared for finding the most feasible process technology for integrated operation of various lignocellulosic bioethanol process configurations using a dynamic modeling framework. The results showed that five of those configurations produced the highest ethanol yields per amount of dry-biomass: SSCF-C_RECY, C_RECY-C_RECY, C_RECY-C and SSCF-FB (0.18, 0.16, 0.14 and 0.13 kg/kg, respectively four of them involving a recycle flow). Sensitivity analysis of the reaction volume with respect to process yield for ethanol has shown the possibility of reducing the number of equipments without compromising the bioethanol production yield.

Acknowledgements

The authors acknowledge the Mexican National Council for Science and Technology (CONACyT, Project # 118903) and the Danish Research Council for Technology and Production Sciences (Project # 274-07-0339) for the financial support on the development of this project.

Appendix A. Supplementary material


References


